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Tin exchanged zeolite as catalyst for direct synthesis of α-amino nitriles under solvent-free conditions

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ABSTRACT

Sn exchanged HBeta zeolite was prepared and characterized by PXRD, surface area, TPD and TEM analysis. The Sn exchanged zeolite was found to be highly efficient catalyst for the direct synthesis of α-amino nitrile from various ketones and aldehydes with amine and trimethyl silylcyanide (TMSCN) under solvent-free condition. Excellent yield of α-amino nitrile (up to 96%) was achieved within 10–120 min at room temperature. The Sn exchanged HBeta zeolite was recovered and reused several times without the loss of its catalytic performance.

1. Introduction

There are intentionally different approaches among the chemists towards the carbon—carbon bond forming reactions. Among these a very elegant and versatile solution is provided through the addition of cyanide to an imine (Modified Strecker reaction) which also represents one of the intrigued methods for preparing α-amino acids [1]. α-Amino nitrile plays a significant role in organic chemistry because of its bifunctional nature, an amino and a nitrile group, thus it offers various synthetic approaches to different classes of natural and bioactive compounds [2]. α-Amino nitrile is also a valuable prebiotic precursor to porphyrins, corrins, nicotinic acid, nucleic acids, safromycin A (anti-tumor potency) and phthalascidin [3]. The versatile synthon α-amino nitriles are prepared by the reaction of aldehydes or ketones [4] with amines in the presence of various cyanide sources such as HCN [3,5], KCN [6,7], TMSCN [8] and Et_2AlCN [9]. Among these TMSCN has emerged as a promising, effective and relatively safer cyanide source [10] for the Strecker reaction. These catalytic systems performed well with aldehydes [11–49] but were not so effective in the case of ketone in most cases. Nevertheless, there are few catalysts reported for the Strecker reaction using less reactive electrophilic ketones [11,21,43–53]. Significant among these are Lewis acid/Brønsted acid catalysts like $Fe(cp)_2{\cdot}PF_6$ [11], PEG [27], sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles [43], sulfonate group anchored on mesoporous silica [44], tin ion-exchanged montmorillonite [45], nanocrystalline MgO [46], NHC-amidate Pd(II) complex [47], Li-trifluoroboronate [48], mesoporous aluminosilicate [49], TMSOTf [50], xanthan sulfuric acid [51], gallium(III)triflate [52], under ambient or high pressure [21,53] and solvent/solvent-free conditions. Although some outstanding catalytic systems have been reported, still there is a plenty of room for improvement, particularly in terms of catalyst recyclability, high catalyst activity at lower catalyst loading and conducting the reaction under solvent-free condition in lesser time. Onaka et al. [45] showed that individually Na-Mont, $Sn(OH)_4$, SnO_2, Sn-MCM-41 and Al-MCM-41 do not catalyze Strecker reaction. However, low to moderate product yields were obtained when SnO_2/silica (7.2%), SnO_2/MCM-41 (22%) and $SnO_2/SiO_2–Al_2O_3$ (37%) were used as catalyst. The best results were however obtained when Sn-Mont (84% in 3 h) was used as catalyst. Exploring the utility of Sn exchanged zeolite as catalyst for this reaction was conspicuously absent despite the fact that zeolites have been extensively used as solid catalyst in various organic transformations [54] and is industrially valuable [55,56] because of its easy synthesis, porous structure with tunable ion exchange capacity. In view of the above and our ongoing interest in developing environment friendly and solvent free protocol for various organic transformations [11,57–59], here we are reporting Sn

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exchanged HBeta zeolite catalyzed Strecker reaction under solvent free condition to get α-amino nitriles in excellent yield (up to 96%) within 10–120 min with an added advantage of recyclability of the catalyst.

2. Experimental

2.1. Materials and methods

X-ray powder diffraction studies at ambient temperature were carried out using a PHILIPS X'pert MPD system in the 2θ range of 5–65° using Cu Kα1 (λ = 1.54056 Å). Surface area of the HBeta zeolite samples were determined by nitrogen adsorption method at 77.35 K was measured using ASAP 2020 (Micromeritics Inc., USA) after activating the sample at 673 K under vacuum. Acidity of the zeolites was characterized by the TPD of NH_3 (Micromeritics, Autochem 2920). The standard procedure for TPD measurement involved the activation of zeolite in flowing He at 723 K (4 h), cooling to 303 K and adsorbing NH_3 from a stream of He–NH_3 (10%), removing the physically adsorbed NH_3 by desorbing in He at 373 K for 1 h and finally carrying out the TPD experiment by raising the temperature of the catalyst in a programmed manner (10 K/min). The TPD curves were deconvoluted into peaks and the areas under the peaks were converted into milliequivalents (mequiv.) of NH_3 per gram of catalyst based on injection of known volumes of the He–NH_3 mixture at similar conditions. Elemental analysis was done on CHNS Analyzer, PerkinElmer model 2400 (USA). FTIR spectra were recorded by PerkinElmer Spectrum GX spectrophotometer (USA) in KBr window. An inductively coupled Plasma-Optical emission spectrophotometer (ICP-OES, Optima 2000 DV, PerkinElmer, Eden Prarie, MN) was used to determine the weight percentage of the tin in the SnHBeta zeolites. Transmission electron microscope (TEM) analysis was done using JEOL, JEM-2100 microscope at 200 kV using carbon coated copper grid. HBeta and tin exchanged HBeta zeolite was dispersed in ethanol and a drop of dispersion was laid on grid for TEM to determine the surface morphology. NMR spectra were recorded on a Bruker F113V spectrometer (200 MHz and 500 MHz, Switzerland) and were referenced internally with TMS. For the product purification flash chromatography was performed using silica gel 60–120 mesh purchased from s.d. Fine-Chem. Ltd., India.

HBeta zeolite having SiO_2/Al_2O_3 ratio of 24 was procured from Zeochem, Switzerland and $SnCl_2{\cdot}2H_2O$ (E. Merck India Ltd., India). $SnCl_4$, trimethyl silylcyanide (TMSCN), 2-methyl benzaldehyde, 3-methyl benzaldehyde, 4-methyl benzaldehyde (all from Merck, Germany), benzaldehyde, 4-methoxy benzaldehyde, 3-methoxy benzaldehyde, 4-fluoro benzaldehyde, 2-fluoro benzaldehyde, 4-chloro benzaldehyde, 1-naphthaldehyde, 2-thiophenecarboxaldehyde, 2-furan-carboxaldehyde, hydrocinnamaldehyde, hexanal, 3-methyl butyraldehyde, aniline, benzyl amine (all from Aldrich, USA), acetophenone, propeophenone, 4-chloro acetophenone, 4-bromo acetophenone, 4-methyl acetophenone, 2-methyl cyclohexanone, 4-methyl cyclohexanone, 2′-acetonaphthone, benzylideneacetone, 2-hexanone (all from ACROS ORGANICS) and benzophenone (s.d. Fine-Chem. Ltd., India) were used as received.

2.2. Catalyst synthesis

Sn cations from aqueous solution were introduced into the highly crystalline HBeta zeolites by the conventional cation exchange procedure [60]. Zeolite samples having different degree of tin exchange were prepared by changing the concentration and solid/liquid ratio during tin exchange. 2.4% SnHBeta and 1.4% SnHBeta samples were prepared by using 0.01 and 0.005 M aqueous solution of $SnCl_2{\cdot}2H_2O$ in the solid/liquid ratio 1:100 respectively at 25 °C under stirring for 24 h. The residue was filtered, washed with hot distilled water, until the washings were free from ions and dried in air oven at 80 °C and calcined at 550 °C for 4 h.

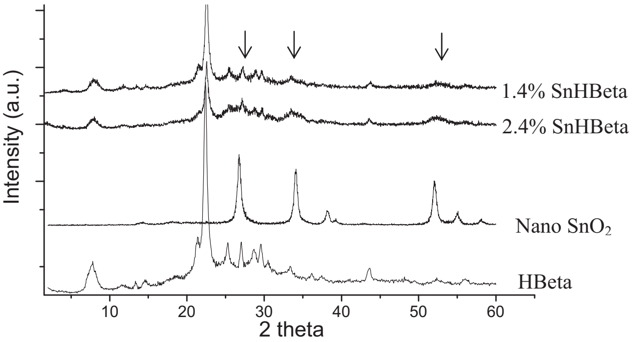


Fig. 1. XRD pattern of HBeta, nano SnO_2 and tin exchanged HBeta zeolites.

An inductively coupled plasma-optical emission spectrophotometry showed that the catalysts 2.4% SnHBeta and 1.4% SnHBeta samples have 2.4 wt% and 1.4 wt% of tin respectively.

2.3. Experimental procedure for the synthesis of α-amino nitrile using Sn-exchange zeolite

The catalyst Sn-exchange zeolite (10 mg for ketones and 5 mg for aldehydes) was taken in a 5 ml round bottom vial and sealed with a rubber septum to which a ketone or an aldehyde (1 mmol) and aniline (1 mmol) were added at room temperature under stirring. To the above stirred solution TMSCN (CAUTION: Toxic! 1.3 mmol) was added in small fractions over a period of 5 min. The progress of reaction was monitored on TLC. After completion of reaction, the catalyst was removed by centrifugation and/or filtration. The solid was washed with methanol. Washings and the filtrate were combined, concentrated and was subjected to flash column chromatography on silica gel (eluted with hexane/ethyl acetate, 90:10) to get the respective α-amino nitriles in good to excellent yield. The purified products were characterized by melting point, IR, microanalysis, ^1H and ^{13}C NMR analysis. Characterization data of some selected products are as follows:

2-Phenyl-2-(phenylamino)propanenitrile (Table 5, *entry 1*): White solid, m.p., 140–142 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ = 1.90 (s, 3H), 4.15 (s, 1H), 6.50 (d, J = 8.2 Hz, 2H), 6.77 (t, J = 7.9 Hz, 1H), 7.08 (t, J = 7.9 Hz, 2H), 7.33–7.45 (m, 3H), 7.60 (d, 2H, J = 8.0) ppm; IR (KBr): 3390, 2929, 2230, 1610, 1522, 1435, 1178, 1090, 756 cm^{-1}.

2-(N-Anilino)-2-phenylacetonitrile (Table 6, *entry 1*): White solid; m.p., 76–78 °C; ^1H NMR ($CDCl_3$ 200 MHz): δ = 4.0 (d, J = 8, 1H), 5.4 (d, J = 8.2, 1H), 6.7 (d, J = 7.6, 2H), 6.9 (t, J = 7.4, 1H), 7.2–7.3 (m, 2H), 7.5–7.5 (m, 3H), 7.5–7.6 (m, 2H) ppm; ^{13}C NMR (50 MHz, CDCl3): δ = 50.9, 114.8, 118.9, 120.9, 130.0, 130.2, 130.3, 134.5, 145.3 ppm; IR (KBr) ν 3338, 3029, 2940, 2237, 1600, 1515, 1497, 1283, 1243, 1114, 924, 753, 693 cm^{-1}.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. X-Ray powder diffraction

The diffraction patterns of the HBeta shows the reflections in the range of 5–35° typically of highly crystalline zeolites. It was observed that on exchange with Sn ion, the intensities of peaks decreased marginally confirming that the zeolite structure is retained (Fig. 1). The X-ray diffraction patters of the Sn ion exchanged zeolite showed the typical peaks of zeolite beta at 2θ

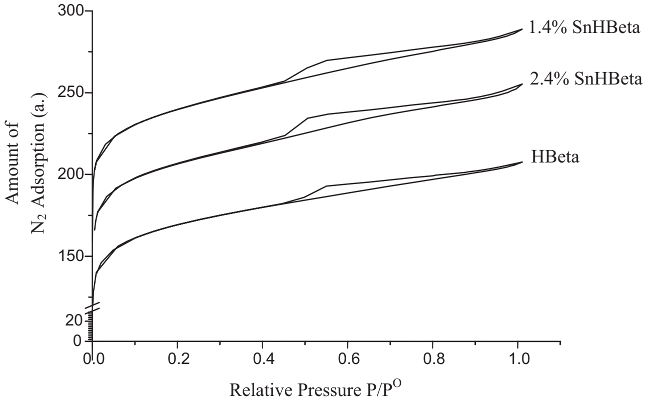


Fig. 2. N_2 adsorption desorption isotherm of HBeta and tin exchanged HBeta zeolites.

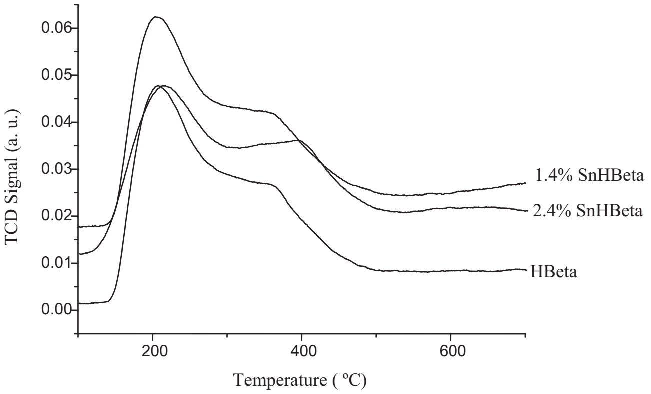


Fig. 3. NH_3 TPD profiles of the tin exchanged HBeta zeolites.

values of 7.25, 7.83, 21.43, 22.42, 25.27, 27.04, 28.79 and 29.55. The decrease in peak intensity is due to loss in crystallinity caused by the HCl released during calcination of tin exchanged zeolite samples. The origin of HCl can be traced to the tin chloride solution used during the metal exchange step. The tin exchanged zeolite samples also show three less intensity broad peaks (shown by down arrow) at $2\theta^\circ$ of 26.5, 33.8 and 51.5 in the XRD pattern assigned to the 1 1 0, 1 0 1 and 2 1 1 plane of poorly crystalline cassiterite phase (No. 00-041-1445) of SnO_2 [60,61]. This shows that in addition to tin exchange, of some amount of SnO_2 crystals are formed during calcinations. However, no peaks were observed for metallic tin and SnO and these features are in line with earlier reported [60] tin exchanged zeolite samples.

Nano-sized SnO_2 that we synthesized for the present study in order to compare its catalytic activity (in Strecker reaction) with Sn-exchanged zeolite samples showed strong peaks at $2\theta^\circ$ of 26.6, 34.0 and 51.8 (Fig. 1).

3.1.2. Surface area and pore size distribution

Micropore and external surface areas of all the zeolite samples used in the present study were determined from t-plot method. The surface area and micropore volume were slightly decreased on tin exchange due to some loss of crystallinity and filling of pores by large tin cations and some SnO_2 nanoparticles formed during calcination in the micropores of zeolite. The observed increase in the external surface area is a reflection of increased amorphous phase of zeolite; however contribution from the deposition of some SnO_2 nanoparticles on the zeolite surface cannot be ruled out (Table 1). The adsorption/desorption isotherm of HBeta and SnHbeta samples (Fig. 2) shows hysteresis loop in the range $P/P^\circ = 0.5–1$, indicating the presence of non-framework intra-particular porosity [62].

3.1.3. Ammonia temperature programmed desorption

The HBeta zeolite contains two types of acidic sites, weak acid sites at around 180 °C and strong acid sites around 326 °C (Table 2). The decrease in desorb ammonia and increase in desorption temperature shows that the amount of these two acidic sites decreases but their strength increases on tin exchange (Fig. 3). The polarizing and inductive effects of tin ions weaken the OH bonds of bridging hydroxyl groups and make them more acidic. The broad peak centered at around 600 °C in all the samples is possibly due to the dehydroxylation of HBeta zeolite [63] (Table 2).

3.1.4. Transmission electron microscopy (TEM) analysis

The photomicrographs obtained by TEM showed well defined ordered porous structure of HBeta zeolite framework in all the samples including tin-exchanged zeolite samples indicating that the zeolite frame work is not destroyed during metal exchange process. Besides, some well-formed tin oxide nanoparticles of less than 5 nm are also visible (mostly on the surface) in both 2.4% SnHBeta (b) and 1.4% SnHBeta (c) which are not found in HBeta zeolite (a) (Fig. 4). TEM photomicrograph of as synthesized nano-SnO_2 (of ~20 nm size) shows morphology similar to the SnO_2 present in tin-exchanged zeolite samples (Fig. 4).

3.2. Catalytic properties of SnHBeta systems

The systematic catalytic study for the synthesis of α-amino nitrile was started using acetophenone and aniline as model substrates (1 mmol scale) with TMSCN as a source of cyanide under

Table 1
Surface area analysis data of Sn-exchange zeolite.

Sample	BET surface area (m^2/g)	Micropore surface area (m^2/g)	External surface area (m^2/g)	Pore volume (cm^3/g)
HBeta	636	451	185	0.209
2.4% SnHBeta	576	363	213	0.170
1.4% SnHBeta	630	403	227	0.188

Table 2
Ammonia temperature programmed desorption data of Sn-exchange zeolite.

Sample	Acidity						
	Temp. (°C)	mmol/g	Temp. (°C)	mmol/g	Temp. (°C)	mmol/g	Total
HBeta	180	0.661	326	0.142	–	–	0.803
2.4% SnHBeta	205	0.307	395	0.092	596	0.015	0.414
1.4% SnHBeta	199	0.379	363	0.043	625	0.010	0.432

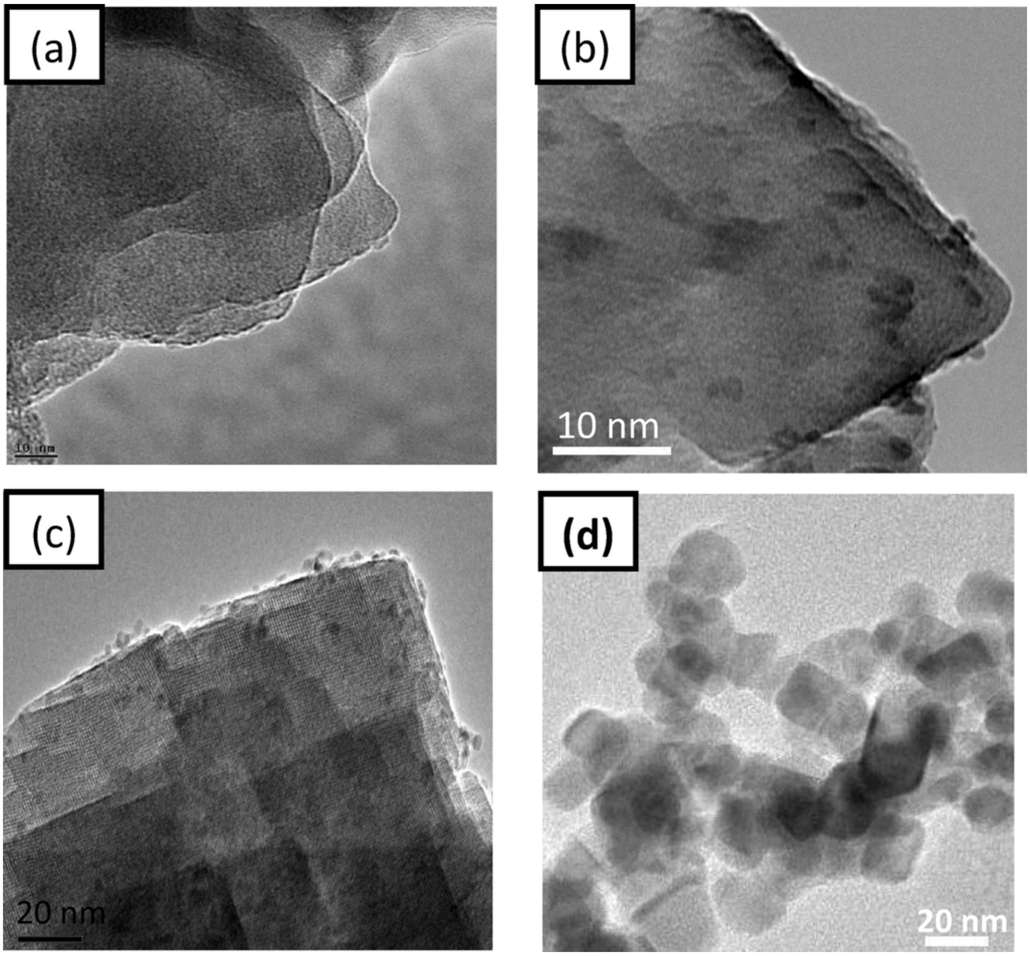
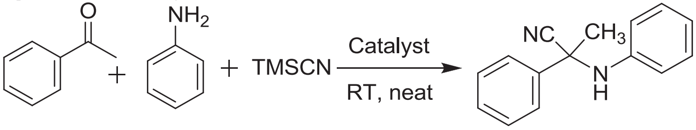


Fig. 4. TEM images of zeolites (a) HBeta, (b) 2.4% SnHBeta, (c) 1.4% SnHBeta, and (d) nano-SnO_2.

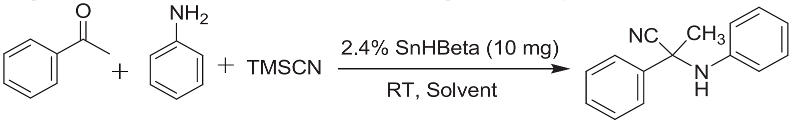
Table 3
Optimization of catalyst for the Strecker reaction.[a]



Entry	Catalyst	Amount of catalyst (mg)	Time (min)	Yield (%)[b]
1	No catalyst	–	60	Trace
2	No catalyst	–	720	60
3	HBeta zeolite	10	75	76
4	2.4% SnHBeta	10	30	93
5	1.4% SnHBeta	10	48	85
6	SnO_2 (commercial)	2.4[c]	60	Trace
7	Nano-SnO_2[d]	2.4[c]	60	Trace
8	HBeta zeolite + Nano-SnO_2 (2.4%) physical mix	10	75	78
9	SnO_2 (commercial)	10	50	85
10	$SnCl_2{\cdot}2H_2O$	2.4[c]	60	Trace
11	$SnCl_2{\cdot}2H_2O$	10	30	82
12	Recycled $SnCl_2{\cdot}2H_2O$	9.5	60	22
13	2.4% SnHBeta	5	65	82
14	2.4% SnHBeta	2	75	82
15	2.4% SnHBeta	20	40	85
16	2.4% SnHBeta	100[c]	45	90
17	SBA-15[e]	10	60	Trace
18	1.1% SnSBA-15	20	60	8[f]

[a] All reactions were carried out at RT using acetophenone (1 mmol), aniline (1 mmol), TMSCN (1.3 mmol).
[b] Isolated yield.
[c] Reaction was carried at 10 mmol scale.
[d] Nano sized SnO_2 was prepared as per the reported procedure [64].
[e] SBA-15 was prepared as per the reported procedure [65].
[f] Calculated by GC.

Table 4
Scope of various solvents for Strecker reaction under optimized catalyst condition.[a]



Entry	Solvent	Time (min)	Yield (%)[b]
1	Solvent free	30	93
2	Methanol	120	82
3	Ethanol	120	83
4	Acetonitrile	120	78
5	Toluene	120	30
6	Chloroform	120	45

[a] All reactions were carried out at RT using acetophenone (1 mmol), aniline (1 mmol), TMSCN (1 mmol) in 2 mL of solvent.
[b] Isolated yield.

solvent free condition at room temperature (Table 3). In the absence of a catalyst only traces of product formation was observed (entry 1) in 60 min, however with extended period (720 min) the desired product was obtained in 60% isolated yield (entry 2). Whereas the same reaction when conducted in the presence of HBeta zeolite (10 mg) of high Brønsted acidity, the desired product was obtained in 76% isolated yield in 75 min (entry 3). Remarkably, the use of Sn^{2+} exchanged zeolite (2.4% SnHBeta, prepared from the 0.01 mmol aqueous solution of $SnCl_2{\cdot}2H_2O$) (10 mg) as catalyst gave the product in 93% yield within 30 min (entry 4). Interestingly, HBeta zeolite with lower Sn^{2+} content (1.4% SnHBeta, prepared from 0.005 mmol aqueous solution of $SnCl_2{\cdot}2H_2O$) gave relatively lower product yield (85%) in longer reaction time 48 min (entry 5). At this point it looked like that Brønsted acid sites (both H and exchanged Sn^{2+}) are responsible for the increased catalytic activity where contribution of Sn^{2+} is relatively more. However, tin exchanged zeolite samples also showed the presence of well distributed nano-sized SnO_2 particles and the possibility of these particles catalyzing (as Lewis acid sites) the reaction cannot be ruled out entirely. To address this issue, this reaction was conducted by using commercial grade SnO_2 (entry 6) and nano-SnO_2 (as synthesized, entry 7) as catalysts and for the sake of fair comparison the tin content of 2.4% was kept constant. Noticeably, in both the cases only trace amount of product formation took place in 60 min. However, a physical mixture of nano-SnO_2 (2.4%) and HBeta zeolite catalyzed this reaction to give the product in 78% yield in 75 min (entry 8). This result is at par with the results obtained with commercial HBeta zeolite sample (entry 3) implying very little or no contribution of SnO_2 in catalyzing this reaction at this Sn loading. However, SnO_2 at higher Sn loadings (10 mg) do catalyze this reaction (entry 9). Further, in order to rule out the possibility of $SnCl_2{\cdot}2H_2O$ (adhered to zeolite) acting as a catalyst by itself, a catalytic experiment with $SnCl_2{\cdot}2H_2O$ at 2.4% Sn loading was conducted that showed only trace of product formation in 60 min (entry 10). This experiment rules out the possiblity of contribution $SnCl_2{\cdot}2H_2O$ at this Sn loading but at higher Sn loading $SnCl_2{\cdot}2H_2O$ (entry 11) also catalyze the reaction appreciably (82% yield in 30 min). It is to be noted here that the activity of $SnCl_2{\cdot}2H_2O$ comes down drastically (22% yield) during recycle experiments possibly due to its instability (hydrolysis) under the reaction condition (entry 12). The results obtained with these sets of experiments clearly indicate that the catalytic activity of well distributed Sn^{2+} ions in exchangeable positions of zeolite cavities is greater than SnO_2 (nano) particles and/or Brønsted acid sites of zeolite.

In view of the above, 2.4% SnHBeta was used as preferred catalyst in our subsequent studies on Strecker reactions to optimize reaction parameters and scope of various substrates. Accordingly, first we varied the catalyst loading in milligrams per 1 mmol of acetophenone as a model substrate. A catalyst loading ranged over 2–20 mg/1 mmol of the substrate was used (entries 13–15) under identical reaction conditions which, revealed that a catalyst loading of 10 mg (entry 4) is optimum to achieve best product yield in shortest reaction time.

At a relatively higher scale (10× 1 mmol), of the representative substrate acetophenone with aniline and TMSCN gave the product in 90% isolated yield in 45 min indicating that the present protocol is scalable (entry 16, Table 3).

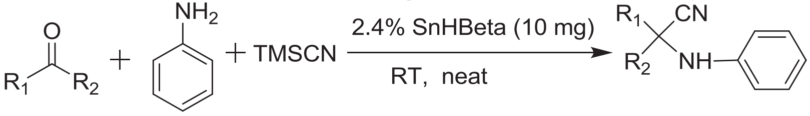
SBA-15 as such does not catalyze the Strecker reaction (entry 17) however, 8% product formation was observed with 1.1% SnSBA-15 sample (entry 18) (TEM image is given as supporting information) which is very low as compared with tin exchanged zeolite samples. Therefore, it can be safely concluded that both bulk and nano-SnO_2 poor catalyst for Strecker reaction with ketonic substrate and the finding is in line with the observations reported in the literature [45].

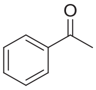
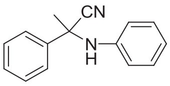
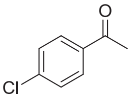
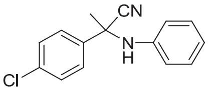
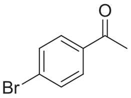
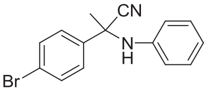
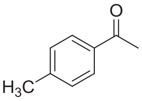
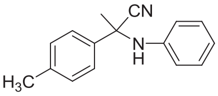
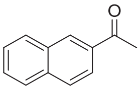
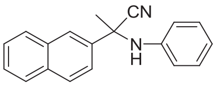
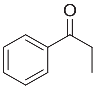
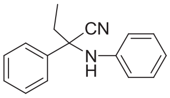
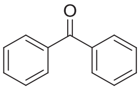
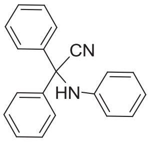
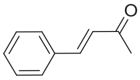
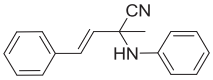
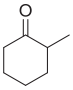
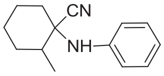
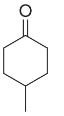
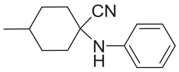
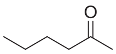
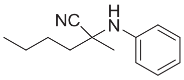
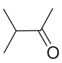
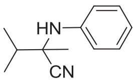
The role of solvent was also assessed in Strecker reaction of acetophenone with optimized amount of the catalyst 2.4% SnHBeta (Table 4). The alcoholic solvents e.g., methanol and ethanol gave 82 and 83% (entries 2 and 3) of corresponding α-amino nitrile in 120 min respectively. Whereas, the same reaction when conducted in acetonitrile, chloroform and toluene afforded the Strecker product in 78, 30 and 45% (entries 4, 5 and 6) yield in 120 min. The results reveal that in the present catalytic protocol some of the solvents e.g., methanol, ethanol and acetonitrile where the mobility of proton (H^+) is more feasible than the solvents like chloroform and toluene can be effectively used. However, the performance of solvent free condition (entry 1) is better both in terms of product yield and shorter reaction time than the same reaction when conducted in the presence of a solvent. This phenomenon is not unusual as solvents are known to compete with reagents on adsorption/catalytic sites [19].

Next, we extended the solvent-free catalytic protocol to various aromatic and aliphatic ketones with aniline and TMSCN using 2.4% SnHBeta as catalyst and the results are summarized in Table 5. It is understood from the results that the alkyl phenyl ketones in general gave very good product yield (entries 1–6; yield, 81–95%) in short time (15–45 min). The reaction was however relatively sluggish (120 min) in the case of benzophenone and α,β-unsaturated ketone e.g., benzylideneacetone (entries 7 and 8) to give the respective products in low yields 30 and 25% respectively. Remarkably, cyclic ketones like 2-Me-/4-Me-cyclohexanone gave good product yield (~80%) in 50 min (entries 9 and 10) but linear or branched aliphatic ketones failed to give any product in 120 min (entries 11 and 12).

This protocol at a very low catalyst loading (5 mg of 2.4% SnHBeta/1 mmol of substrate) worked well for various aldehydes having variable electronic and steric features to give respective products in excellent isolated yields (80–96%) in 10–20 min

Table 5
Direct Strecker reaction of various ketones in the presence of 2.4% SnHBeta as a catalyst with aniline and TMSCN under solvent free condition.[a]

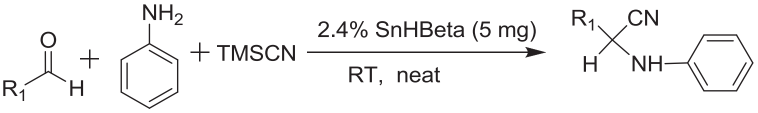


Entry	Ketone	Time (min)	Product	Yield (%)[b]
1		30		93
2		45		86
3		45		81
4		15		88
5		20		95
6		35		89
7[c]		120		30
8		120		25
9		50		80
10		50		82
11		120		00
12		120		00

[a] All reactions were carried out at RT, using 2.4% SnHBeta as catalyst (10 mg), ketone (1 mmol), aniline (1 mmol) and TMSCN (1.3 mmol).
[b] Isolated yield.
[c] Reaction carried out at 60 °C.

(Table 6). Aldehydes as diverse as aromatic with electron withdrawing and donating substituents at ortho, meta and para positions (entries 1–10), heterocyclic (entries 11 and 12) and aliphatic aldehydes (entries 13–15) have undergone Strecker reaction with aniline and TMSCN very efficiently. Distinctly, para substituted aldehydes have reacted faster than their ortho or meta counter parts of methyl substituted (entries 2–4), methoxy (entries 5 and 6) and fluoro substituted benzaldehyds (entries 7 and 8). This protocol also work well (yield 92% in 20 min) in the Strecker reaction of benzaldehyde with benzylamine and TMSCN, as demonstrated at entry 16. Although, catalyst-free sequential addition of an aromatic aldehyde, amine and TMSCN has been reported earlier to undergo Strecker reaction efficiently, its one-pot version gave the product in low yields (0–39%) [46]. One-pot Strecker reaction usually happens efficiently only in the presence of a catalyst.

Table 6
Direct Strecker reaction of various aldehydes in the presence of 2.4% SnHBeta as a catalyst with aniline and TMSCN under solvent free condition.[a]



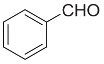
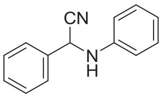
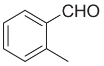
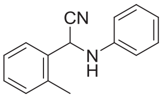
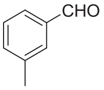
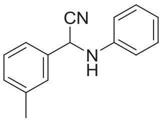
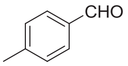
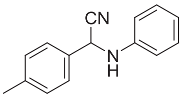
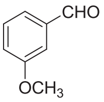
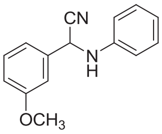
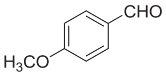
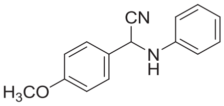
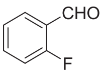
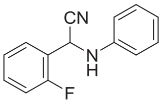
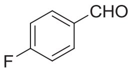
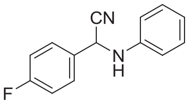
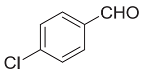
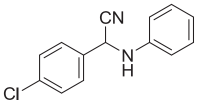
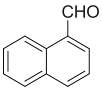
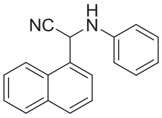
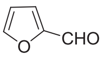
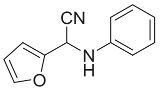
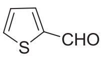
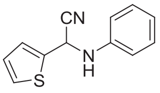
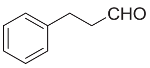
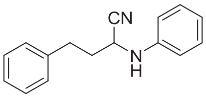
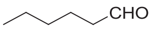
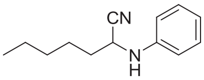
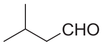
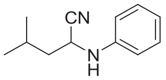
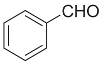
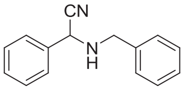
Entry	Aldehyde (R)	Time (min)	Product	Yield (%)[b]
1		10		96
2		15		93
3		15		91
4		10		96
5		15		91
6		10		94
7[c]		10		92
8		10		95
9		15		93
10		15		91
11		10		90
12		10		91
13		15		89
14		20		80

Table 6 (*Continued*)

Entry	Aldehyde (R)	Time (min)	Product	Yield (%)[b]
15		20		88
16[c]		20		92

[a] All reactions were carried out at RT, using 2.4% SnHBeta as catalyst (5 mg), aldehyde (1 mmol), aniline (1 mmol) and TMSCN (1.3 mmol).

[b] Isolated yield.

[c] Reaction carried out using benzyl amine.

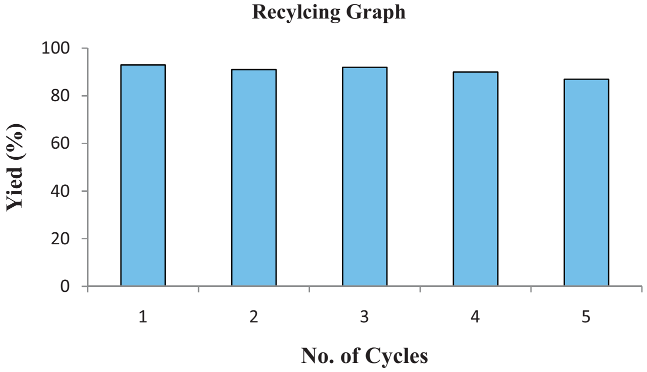


Fig. 5. Recycling data using 2.4% SnHBeta as a catalyst with acetophenone (1 mmol), aniline (1 mmol) and TMSCN (1.3 mmol).

3.3. Catalyst recycling

Fig. 5 shows the recycling data of the catalyst 2.4% SnHBeta for the Strecker reaction using reactants acetophenone, aniline and TMSCN at room temperature under solvent free condition. After the first catalytic run, the product was dissolved in methanol and the catalyst was separated by first centrifugation followed by filteration. The recovered catalyst was dried and activated at 200 °C for 2 h before its reuse in subsequent catalytic runs. The result reveals that the catalyst 2.4% SnHBeta, worked well for five tested cycles without any significant loss of activity and efficiency. The TEM and ICP analysis of the recovered catalyst (after first use) showed no loss in its textural property and tin content. This shows that the catalyst 2.4% SnHBeta is stable and rugged with no metal leaching under our reaction conditions.

4. Conclusion

In conclusion we have display that Sn ion exchange zeolite is a highly active heterogeneous solid catalyst for the direct synthesis of α-amino nitrile (yield up to 96%) under mild and solvent free reaction condition. Various experimental results led us to conclude that the Brønsted acidity of virgin zeolite and exchanged Sn^{2+} sites are synergistically accelerating the Strecker reaction of all the substrates used in general but ketones in particular. Although the catalyst 2.4% SnHBeta contains well distributed SnO_2 particles, controlled experiments have suggested that its role in catalyzing Strecker reaction in the present system is negligible. This protocol also worked well with a variety of aldehydes as substrate to give products in up to 96% yield in 10–20 min. The catalyst is easily recoverable and recyclable (studied up to 5 cycles) and scalable (tested at 10 mmol substrate scale) without any loss in its performance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2012.01.001.

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